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EVALUATION OF GYPSUM CRYSTALLIZATION FOR LIMESTONE FLUE GAS DESULFURIZATION

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16. ABSTRACT The paper gives results of pilot plant tests using a double draw-off crystallizer as the hold tank to improve the gypsum dewatering properties of a forced oxidation limestone flue gas desulfurization process. A hydroclone was used as the size classification device for solids separation and fines removal. Compared with a mixed tank crystallizer, the double draw-off crystallizer resulted in a 45% reduction in free moisture within the filter and a 58% increase in filtration rate.

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ABSTRACT

Pilot plant tests have been conducted using a double draw-off crystallizer as the hold tank to improve the gypsum dewatering properties of a forced oxidation limestone flue gas desulfurization process. A hydroclone was used as the size classification device for solids separation and fines removal. Compared with a mixed tank crystallizer, the double draw-off crystallizer resulted in a 45% reduction in free moisture within the filter cake and a 58% increase in filtration rate.

INTRODUCTION

Gypsum crystallization is an important unit operation for a forced oxidation limestone flue gas desulfurization (FGD) process, because the gypsum dewatering properties can be significantly affected by crystal shape and size distribution. Good dewatering properties not only ease the liquid/solid separation, but also decrease the water loss and waste disposal load. Furthermore, good dewatering properties can also reduce the free moisture of the filter cake which is an important quality specified by potential gypsum users - wallboard manufacturers.(1)

Conventionally, a mixed tank (Figure 1(a)) has been used as the crystallizer for limestone FGD systems.(2) Computer simulation and laboratory experiments indicated that the gypsum crystal size distribution can be changed by modified crystallizer operation which accelerates the removal of fine crystals.(3) The results of accelerated fines removal should be increased production of large crystals and improved gypsum dewatering properties. This is an achievable goal because, with fewer fines present in the crystallizer, the total crystal surface area is decreased and the higher supersaturation can then increase the deposition on the larger crystals still in the crystallizer. This concept can be implemented by a double draw-off (DDO) crystallizer as shown in Figure 1(b). The DDO crystallizer contains a size-classification zone or ancillary size-classification devices (e.g., wet screens, hydroclones, and elutriators). The fine crystal removal rate can be accelerated by increasing the overflow and/or decreasing the underflow.

In order to evaluate the effectiveness of DDO operation on improving the gypsum dewatering properties, pilot plant tests sponsored by the U. S. Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory (AEERL) were conducted. This paper summarizes the test results and compares them with theoretical predictions.

THEORETICAL BACKGROUND

Crystal Size Distribution(4)

When the mixed tank crystallizer is operated under steady state conditions, a specific and very simple form of crystal size distribution can be deduced from the solution of a mathematical model with population balance. Assuming the crystal linear growth rate to be independent of crystal size, the model predicts a linear relationship between the crystal size and the logarithmic value of population density* as shown in Figure 2(a). The weight distribution that results from the population balance model can be obtained directly by weighting the population density by the cube of the crystal size. The typical cumulative and differential weight distribution curves are shown in Figures 3(a) and 4(a), respectively.

The typical population density of a DDO crystallizer, as predicted by the population balance model, is also shown in Figure 2(a). It is seen that small crystals undergo a very rapid decay along a very steep slope until the maximum size of crystals in the fine trap occurs; thereafter, the decay proceeds at a different rate due to mixed product removal. Use of the DDO crystallizer can result in a larger average crystal size as shown in Figure 3(a). Figure 4(a) compares the differential weight distributions for the mixed tank and DDO crystallizers. Note that a bimodal distribution is indicated for the DDO crystallizer in constrast to the unimodal one in the mixed tank crystallizer.

Gypsum Crystallization Kinetics

Etherton(5) conducted a series of gypsum crystallization kinetics studies using a 1-liter glass vessel called a mini-nucleator. Etherton's research

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* Population density is defined as the number of crystals per unit volume of slurry per incremental size range.

found that the following equations correlated his nucleation/growth rate data for gypsum crystals:

$$B^\circ = \exp(16.72)\ G^{1.48} M_T^{1.27} \quad (1)$$

$$G = \exp(13.11) S^{2.226} \quad (2)$$

where B° is the nucleation rate in number/cm^3-min., G is the linear growth rate in μm/min., M_T is the insoluble solids concentration in the slurry in g/cm^3, and S is the supersaturation in g/cm^3.

Equations (1) and (2) were used in a computer simulation (Mark V) developed at the University of Arizona to predict the size distribution of gypsum crystals.[6] Using the computer model, a parametric study was conducted to simulate the gypsum crystal size distribution in DDO crystallizers. Operating parameters studied included DDO ratio (the ratio of crystallizer overflow to underflow), slurry retention time in the DDO crystallizer, crystallizer slurry insoluble solids concentration, and classification size cut. The results predicted that an increase in the DDO ratio will decrease the growth rate (G) and increase the nucleation rate (B°), the slurry solids concentration (M_T), and the average crystal size.

Increasing the DDO ratio speeds removal of the fines (crystals smaller than the classification size cut) and increases the retention time of the product crystals. This increases the slurry insoluble solids concentration and the average crystal size because the retained crystals grow to larger sizes. Figure 5 shows the computer simulation results and also shows the size of the crystals in the product as a function of the classification size cut. When the classification size cut is greater than 50 μm, the product size decreases with increasing classification size cut. The changes of product size are not significant when the classification size cut is less than 50 μm. The product sizes are more sensitive to classification size at the higher DDO ratios than at the lower DDO ratios.

Another parameter studied with the computer model was the crystallizer slurry solids concentration. According to the model, the crystal growth rate should decrease with increasing slurry solids concentration because of the decreasing supersaturation. However, the product sizes still increase because the longer solids retention time overcompensates for decreasing supersaturation.

The effect of slurry retention time, the fourth parameter studied, can be deduced from the nucleation/growth rate equations. As shown by Equation (1), the general form of the nucleation/growth rate equation can be expressed as,

$$B^\circ = c\, G^i M_T^j \qquad (3)$$

where c is a constant. For positive values of (i-j), the average product size increases with increasing retention time. For negative values, the size increases with decreasing retention time. Since (i-j) for gypsum is positive, as indicated by Equation (1), a longer retention time should lead to a desired increased average product size.

PILOT PLANT TESTING

Six tests (Table 1) were conducted with the EPA AEERL's FGD pilot plant.[7] The scrubber was a three-stage mobile bed absorber with 7.5 m^3/min. (0.1 MW) flue gas capacity. No fly ash was present in the flue gas, which was drawn from a gas-fired boiler and injected with pure SO_2 to maintain a 2500 ppm SO_2 concentration in the flue gas during the test. The base case, established by run CR-0, used a single mixed tank as the crystallizer to simulate the conventional forced oxidation FGD system. The DDO crystallization tests were performed during runs CR-1 to CR-5 with the process scheme shown in Figure 6. A hydroclone was used as the size classification device, and crystal size separation was achieved by recycling the hydroclone underflow to the hold tank (crystallizer) and forwarding the hydroclone overflow to the thickener.

The gypsum crystal size distributions were measured by a Coulter Counter for crystals smaller than 45 μm and by wet screen analysis for crystals larger than 45 μm. Gypsum dewatering properties were characterized by slurry settling rate, filter cake free moisture concentration, and filtration rate. The settling rate was taken as the average (of the initial 3-minute period) descent rate of the meniscus between clear supernate and the turbid zone of slurry samples collected in a 100-ml graduated cylinder and observed under quiescent conditions. The filter cake free moisture concentration was taken as the weight difference before and after drying in a microwave oven for 10 minutes.

RESULTS AND DISCUSSION

Pilot plant data (Table 1) indicate that the dewatering properties of gypsum can be improved by replacing the conventional hold tank of wet lime/limestone FGD scrubbers with a DDO crystallizer. Compared with the base case (mixed tank crystallizer, run CR-0), the DDO crystallizer (run CR-1) resulted in increases of the hold tank slurry settling rate from 4.5 to 6.7 cm/min. and the filtration rate from 480 to 760 kg/hr-m^2, and a decrease of filter cake free moisture concentration from 20 to 11%.

Crystal size distribution by Coulter Counter and wet screen analyses showed a bimodal weight distribution from the DDO crystallizer (Figure 4(b)) as predicted by the population balance model (Figure 4(a)). The cumulative weight distribution data (Figure 3(b)) showed substantial differences between runs CR-0 and CR-1 in crystal sizes larger than 30 μm. With the DDO crystallizer, more than 40% of the solids were larger than 30 μm, and over 35% were larger than 50 μm. With the mixed tank crystallizer, less than 1% of the crystals were larger than 30 μm, and no crystals larger than 50 μm were detected. Figure 2(b) compares the population densities derived from crystal size distribution data. As predicted by the population balance model (Figure

2(a)), the population densities of runs CR-0 and CR-1 can be correlated by a single straight line and two straight lines, respectively. However, a discontinuity exists in the population density of the pilot DDO crystallization data (run CR-1). This discontinuity could be partially attributed to the analytical techniques used for crystal size distribution measurement since a Coulter Counter was used for particles smaller than 45 μm and wet screening was used for particles larger than 45 μm where the discontinuity occurs.

Figure 7 shows that effective crystal size separation was achieved by the hydroclone. No crystals larger than 40 μm were found in the hydroclone overflow. On the other hand, more than 60% of the solids were larger than 40 μm in the underflow. However, the fact that about 40% of the solids in the hydroclone underflow were smaller than 40 μm indicates that the hydroclone used does not have a sharp classification size cut as assumed in the population balance model. This less-than-ideal size classification might also have contributed to the discontinuity of the pilot DDO population density shown in Figure 2(b).

Parametric tests were also conducted in the pilot plant to evaluate the effects of the DDO ratio, hydroclone size cut, slurry solids content, and crystallizer residence time. One run (CR-2, Table 1) was made with the DDO ratio increased from 3.5 to 10.0. Based on the population balance model (Figure 5), increasing the DDO ratio should result in larger crystals and better solids dewatering properties. However, the pilot plant data indicated that filter cake free moisture concentration increased from 11 to 15% when the DDO ratio was increased from 3.5 to 10.0. Correspondingly, the slurry solids settling rate and filtration rate decreased. The discrepancy between pilot plant data and theoretical model predictions is believed to be due to

the inability of the thickener to respond to the high DDO ratio. Since the work load of the thickener increased substantially with the increased DDO ratio, it is likely that the design capacity of the thickner was exceeded during the pilot plant testing. As a result, fine particles were carried over in the thickener overflow and returned to the hold tank, thus reducing the effectiveness of the DDO fines removal.

Run CR-3 used a 1.92-cm vortex finder hydroclone to replace the 0.63-cm hydroclone used in previous runs to determine if the classification size cut of the hydroclone increases with a larger vortex finder as predicted by theory. Data in Table 1 show that, after the DDO ratio was restored to 3.5, the slurry settling rate attained was 6.5 cm/min., the filter cake free moisture was 11%, and the filtration rate reached 770 kg/hr-m^2. Compared with the results of run CR-1, no significant effects of classification size change were obtained in the pilot plant testing. Since it is likely that the classification sizes of the two hydroclones tested are within the range of 30 to 60 μm, the average gypsum product size is probably not significantly affected by the classification sizes in this range at the DDO ratio of 3.5 as illustrated by Figure 5.

Both population balance model and gypsum crystallization kinetics indicate that decreasing the slurry solids concentration and residence time should have negative effects on the dewatering properties of the product solids. Comparing runs CR-1 and CR-4, the filter cake free moisture concentration (see Table 1) increased from 11 to 17% when the slurry solids were decreased from 15 to 5%. Correspondingly, the filtration rate decreased from 760 to 630 kg/hr-m^2. On the other hand, when the DDO crystallizer residence time was reduced from 10 minutes in run CR-1 to 5 minutes in run CR-5, the settling rate dropped from 6.7 to 6.0 cm/min. and the filter cake

free moisture increased from 11 to 15%. Therefore, the pilot plant data confirmed that the gypsum dewatering properties should improve with increased residence time and/or slurry solids concentration. Similar results were also reported earlier by TVA in Shawnee prototype testing.(8)

SUMMARY

Pilot plant testing (0.1 MW) has demonstrated that a DDO crystallizer can improve the gypsum dewatering properties of a forced oxidation limestone scrubber. Compared with a mixed tank crystallizer, the DDO crystallizer resulted in the production of gypsum crystals larger than 50 μm, increased slurry settling and filtration rates, and decreased filter cake free moisture concentration.

The hydroclone was found to be an effective size classification device for gypsum crystals. The separation of the fines (crystals smaller than 20 μm) from the crystallizer slurry was achieved although the separation efficiency was less than 100%. Two different vortex finders, which should give two different hydroclone classification sizes, were tested, but no significant effects on gypsum dewatering properties were detected using these vortex finders.

To produce large gypsum crystals, long crystallizer solids residence time and high slurry solids concentration are desirable. Theoretically, a high DDO ratio favors the growth of large crystals. Pilot plant data showed that the high DDO ratio should be considered in thickener design to support formation of large crystals.

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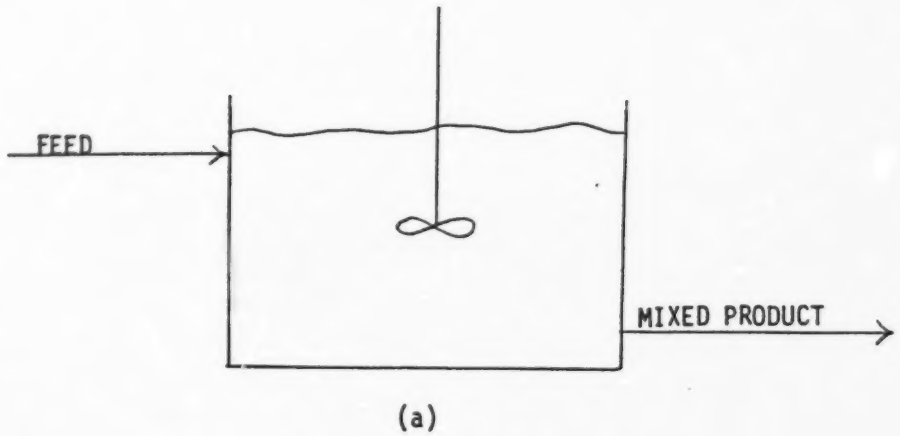
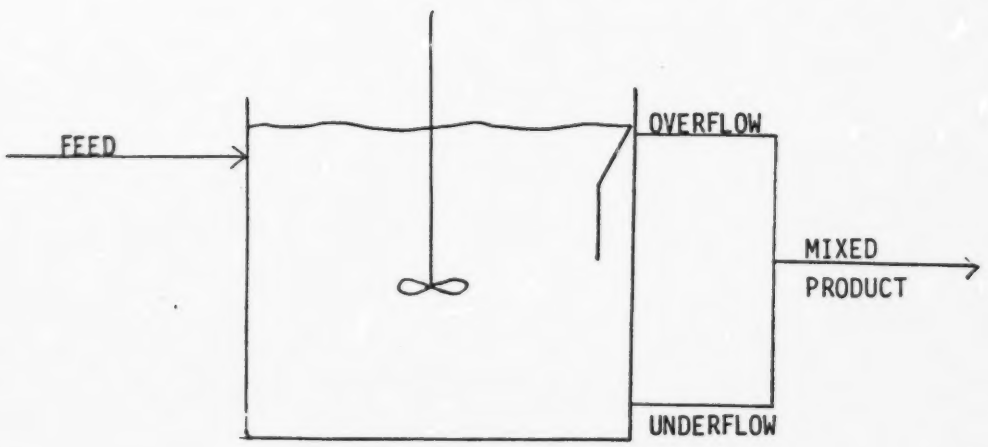
TABLE 1. RESULTS OF CRYSTALLIZATION TESTS

Run	CR-0	CR-1	CR-2	CR-3	CR-4	CR-5
Double draw-off ratio	0	3.5	10.0	3.5	3.5	3.5
HC[a] vortex finder, cm	-	0.63	0.63	1.92	0.63	0.63
HT[b] slurry solids, wt. %	15	15	15	15	5	15
HT residence time, min.	10	10	10	10	10	5
Slurry settling rate, cm/min.	4.5	6.7	5.5	6.5	8.8[c]	6.0
Filter cake free moisture, wt. %	20	11	15	11	17	15
Filtration rate, kg/hr-m^2	480	760	680	770	630	690

[a]Hydroclone
[b]Hold tank
[c]This apparent increase in settling rate was caused by decreased slurry solids concentration

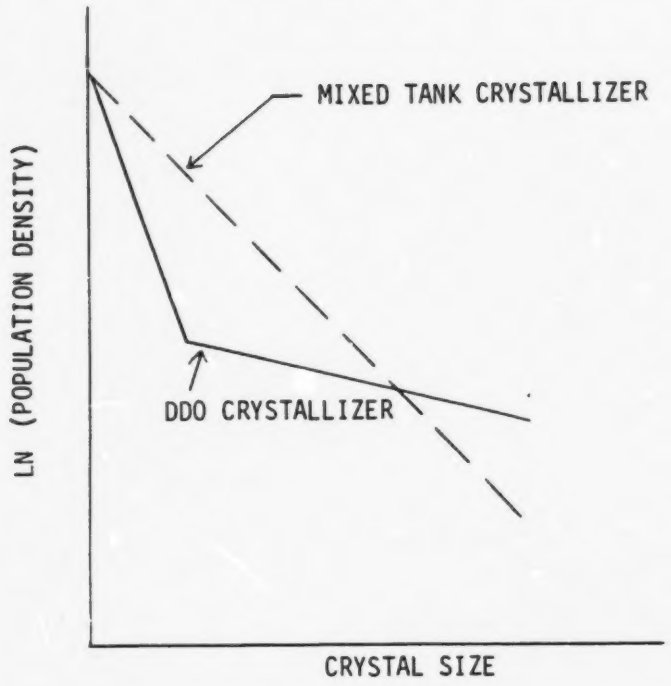


(a)

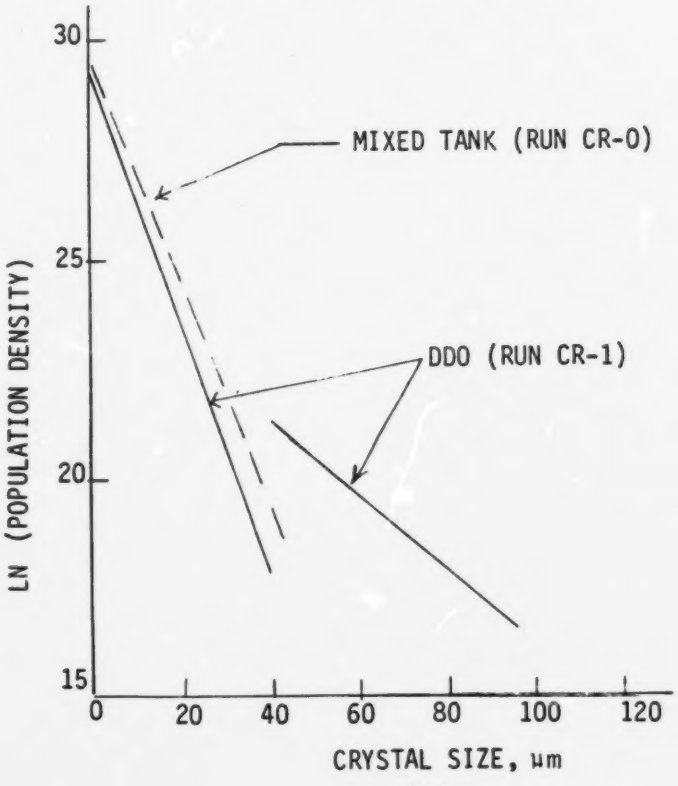


(b)

FIGURE 1. Schematic representation of (a) mixed tank crystallizer and (b) double draw-off crystallizer.

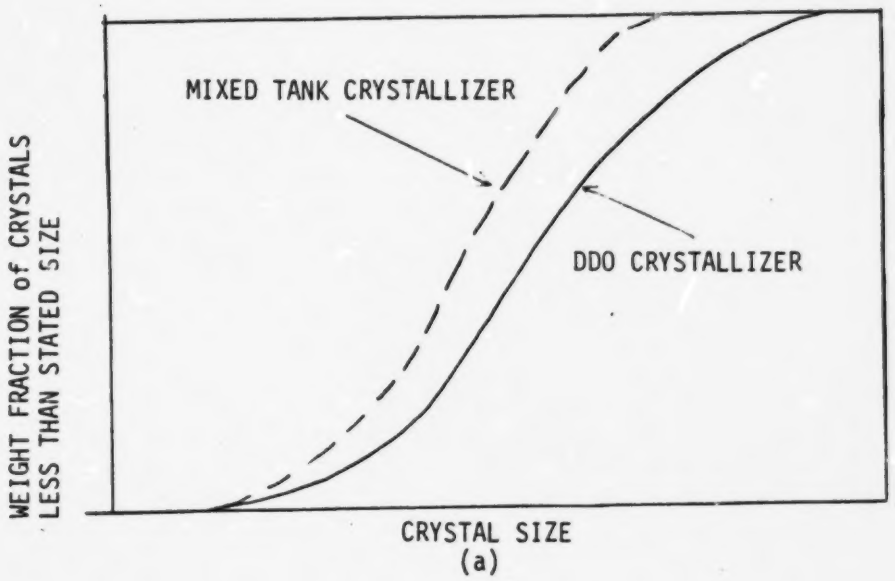


(a)

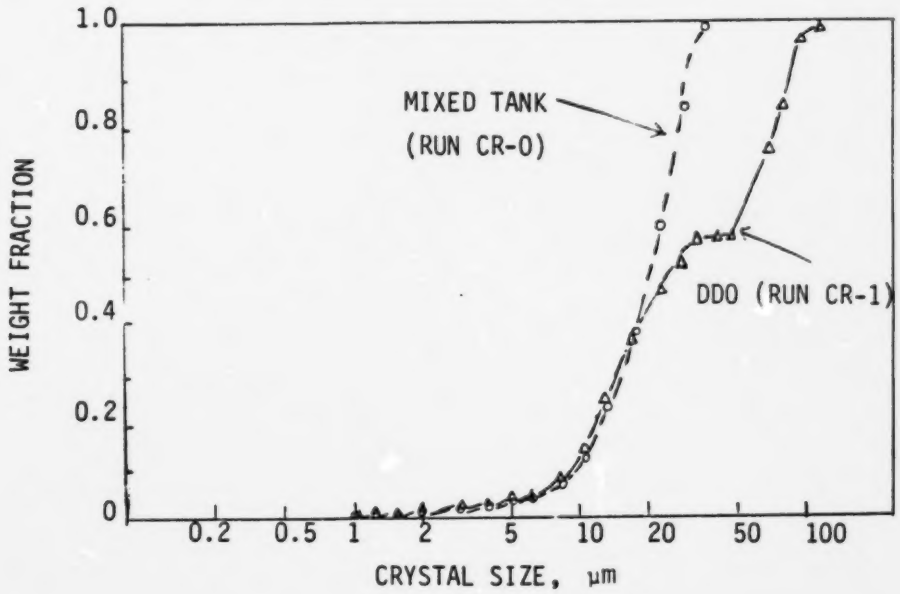


(b)

FIGURE 2. Comparison of population densities from (a) population balance model and (b) pilot plant data.

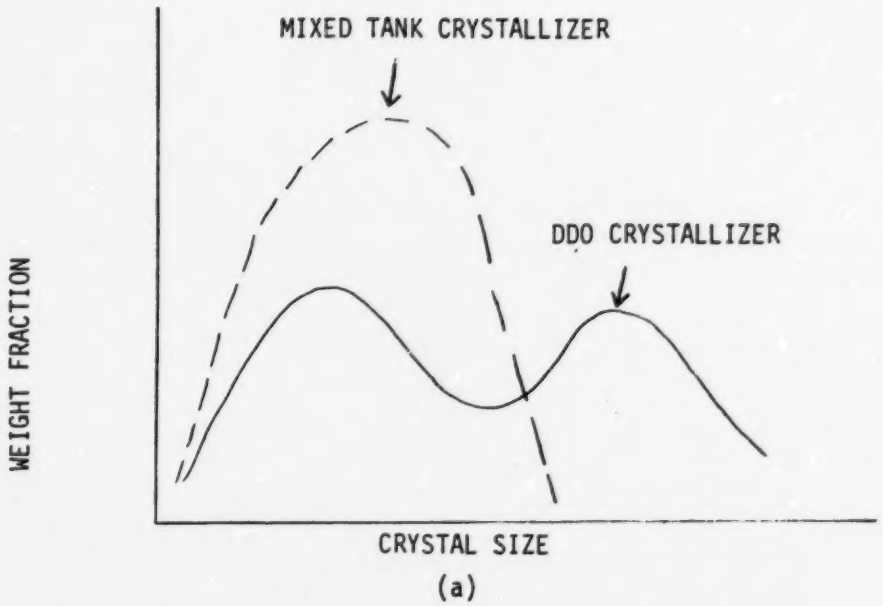


(a)



(b)

FIGURE 3. Comparison of cumulative weight distribution curves derived from (a) population balance model and (b) pilot plant data.



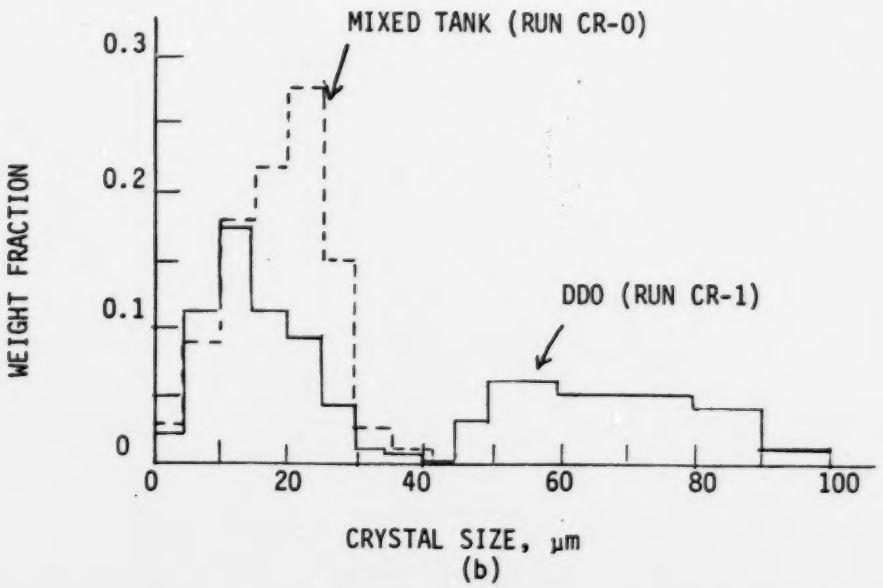


FIGURE 4. Comparison of differential weight distribution derived from (a) population balance model and (b) pilot plant data.

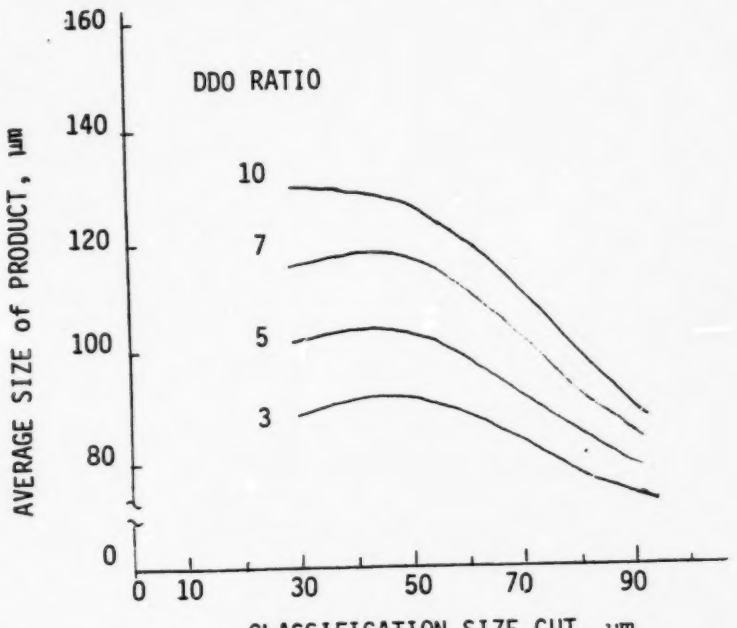


FIGURE 5. Average size of product as a function of classification size cut and DDO ratio.

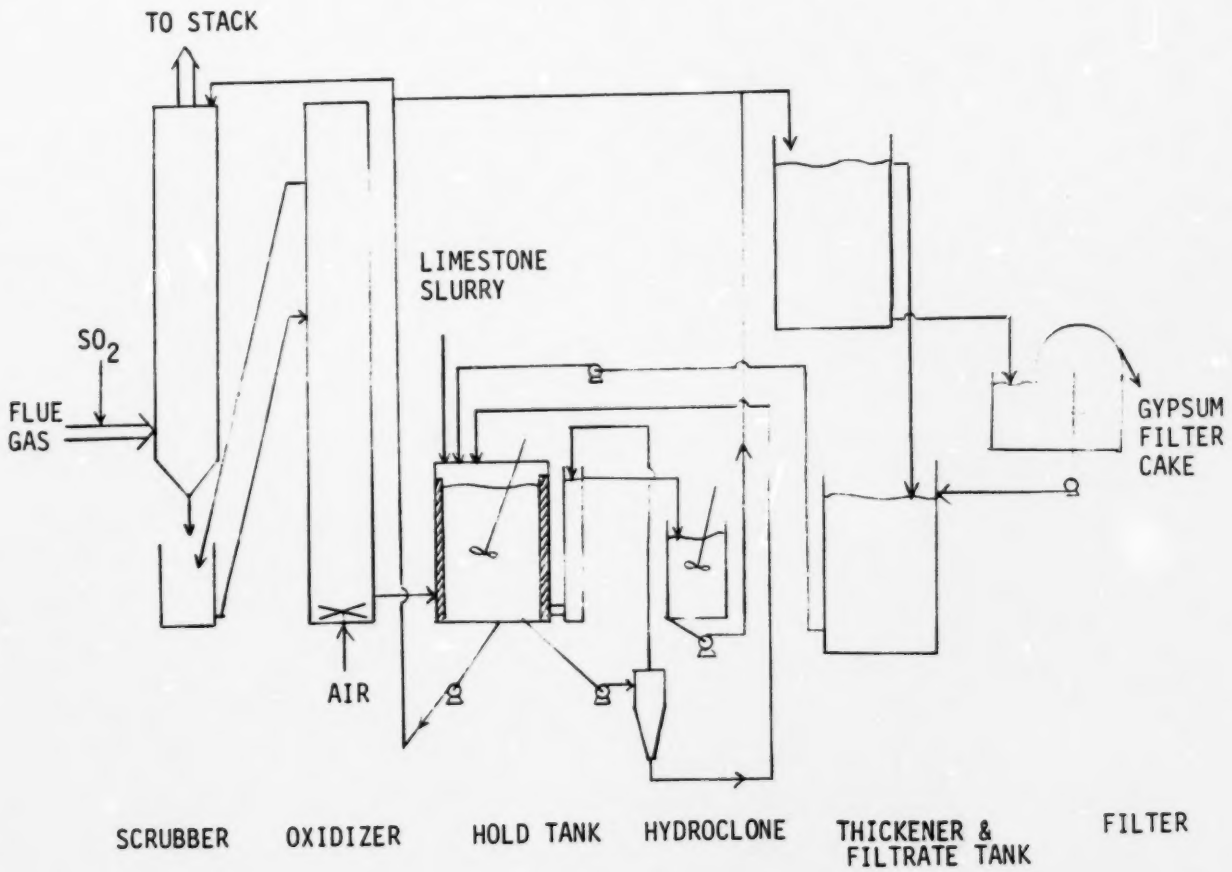


FIGURE 6. Flow diagram of the forced oxidation limestone scrubber with the double draw-off (DDO) crystallizer.

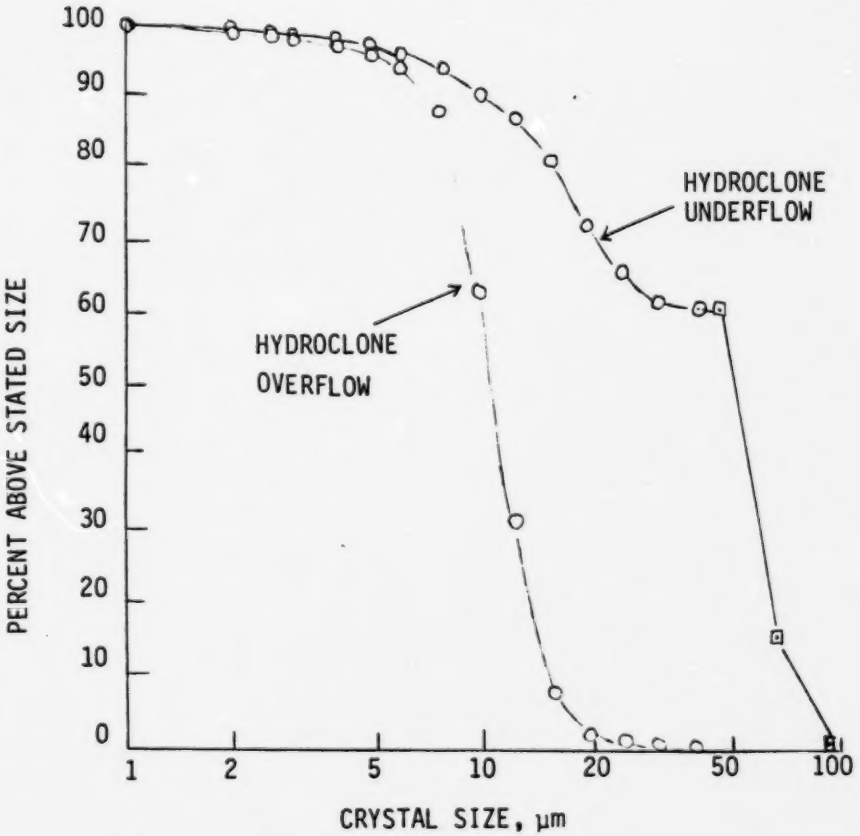


FIGURE 7. Comparison of crystal size distributions in hydroclone overflow and underflow.